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“New Protonated and Anhydrous Chalcogenide Glasses”

by

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Presented at the Gordon Research Conference on

“Fuel-Cells 2001”, Bristol, Rhode Island.

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13. Abstract:

While hydrated electrolytes exhibit high proton conductivities, their use is limited by significant methanol cross-over, mechanical stability and temperatures below 100°C. These limitations can be overcome by synthesizing anhydrous proton conducting materials. In this direction we are investigating the development of anhydrous proton conductors. Protonated (and anhydrous) chalcogenide glass and glass-ceramic materials have been prepared for the first time. These materials open a new choice for the development of fast proton conducting (FPC) electrolytes intended for electrochemical applications, fuel cells in particular. These FPC materials, with proper addition of dopants, are expected to have high proton motion and better thermal stability than polymeric electrolytes.

The protonated materials were prepared in three steps. First  $B_2S_3$  glass was prepared from the elements. A  $B_2S_3$  melt was bubbled with  $H_2S(g)$  and thioboric acid crystals ( $HBS_2$ ) were obtained. Finally,  $HBS_2$  was used as a precursor for the preparation of different glass and glass-ceramic materials, of varying compositions, by adding (i)  $B_2S_3/GeS_2$ .

14. Subject terms: new protonated glasses, thioboric acids, preparation, IR, Raman, NMR.

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# New Protonated and Anhydrous Chalcogenide Glasses

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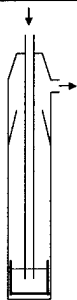
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## MOTIVATION

Hydrated electrolytes have limited applications above 100°C and problems of methanol cross-over and mechanical stability occur. Anhydrous proton conducting materials can overcome these problems. Chalcogenide glasses are promising host materials for fast proton conduction (FPC). We are investigating:

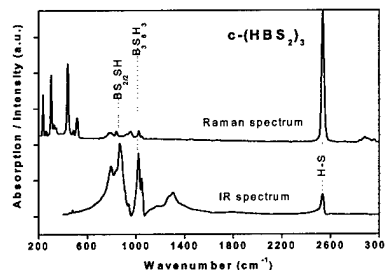
- Preparation of anhydrous protonated chalcogenide glassy materials.
- Achieving FPC in these materials with good thermal stability.
- Fuel cell development based on these anhydrous-FPC materials.



## PREPARATION

- $2B + 3S \rightarrow B_2S_3$  (glass) - at 850 °C for 12 hrs in sealed carbon-coated silica tube.
- $(3/2)B_2S_3 + (3/2)H_2S \rightarrow (HBS_2)_3$  - (crystalline) -  $H_2S$  gas bubbled in  $B_2S_3$  melt (at 500 °C with a  $H_2S$  flow of ~ 6 ml/min) and the condensed vapor  $(HBS_2)_3$  collected.  
-This is a new method to prepare  $(HBS_2)_3$  and only requires lower temperatures.

## IR and Raman Spectra of $(HBS_2)_3$



Trimer Units  
 $(HBS_2)_3$   
6-membered rings

- (a)  $HBS_2 + B_2S_3 \rightarrow H_2S \cdot B_2S_3$  (glass & glass-ceramics).
- (b)  $HBS_2 + GeS_2 \rightarrow H_2S \cdot B_2S_3 \cdot GeS_2$  (glass-ceramics).
- (c)  $HBS_2 + S \rightarrow H_xB_yS_z$  - (ceramics)

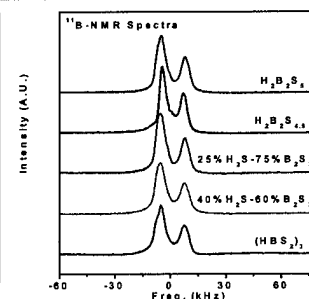
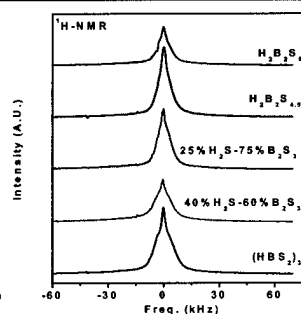
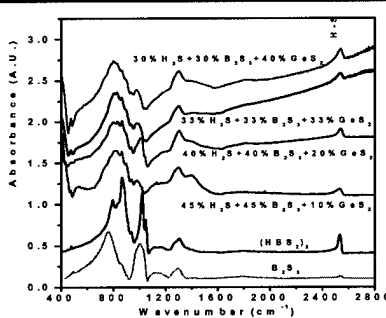
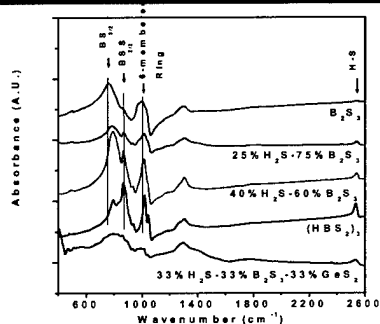
Fine powders of starting materials were mixed and sealed under vacuum in a silica tube. The sealed tube was heated to 300 °C to 550 °C. Glasses and glass-ceramic samples were obtained by quenching the melt in the silica tub.

## IR Spectra: $(HBS_2 + B_2S_3)$

## $(HBS_2 + GeS_2)$

## $^1H$ -NMR Spectra

## $^{11}B$ -NMR Spectra



## DISCUSSIONS

The H-S bonding in the IR spectra signifies the presence of protons in the materials. The 6-membered-ring modes ( $1000\text{cm}^{-1}$ ), are also observed in the protonated glasses. The trigonal modes ( $800\text{cm}^{-1}$ ), are present in all the samples. This indicates that no trigonal to tetrahedral conversion occurs in the samples with the addition of  $H_2S$ . The 6-membered-ring modes, weaken upon addition of  $GeS_2$ . Higher  $H_2S$  concentration are achieved by adding  $GeS_2$ .

$^1H$ -NMR confirms the presence of protons in the glass and glass-ceramic materials. The  $^{11}B$ -NMR shows a resonance peak corresponding to trigonal coordination in all samples, as in IR.

## CONCLUSIONS

New anhydrous protonated glassy materials have been prepared. The present materials opens a new choice for glass-ceramic research. These materials with suitable modifications are expected to have good proton conduction and better thermal stability. They may be better alternatives for conventional hydrous proton conducting materials.

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